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Tenkých vrstev a nanostruktur

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TÉMA

Carotenoid photophysics. Rich excited-state properties of seemingly simple molecules

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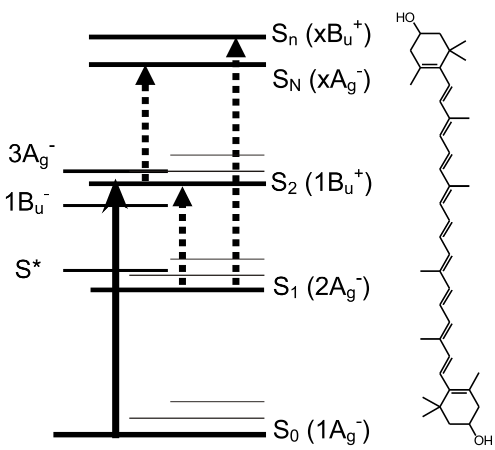

Carotenoids are, along with chlorophylls, the most abundant pigments found in Nature. The diversity of carotenoid functions is unmatched by any other class of natural pigments and is directly related to their unique spectroscopic properties resulting from a structure of carotenoid molecule. The central pattern repeated in all carotenoids is a backbone consisting of alternating single and double carbon bonds that forms a conjugated p-electron system responsible for most of the spectroscopic properties of carotenoids. The bright yellow-orange color of carotenoids is caused by a strong transition to the excited state called S2. Due to symmetry reasons, the transition to the lowest excited state (S1) is forbidden, thereby restricting observable absorption or fluorescence. After excitation, the S2 population relax to the S1 state within a few hundreds femtoseconds, while the lifetime of the S1 state varies between 1-300 ps depending on conjugation length of the carotenoid [1]. This standard picture, known since the dawn of femtosecond time-resolved techniques, has been significantly modified during the past decade [1,2]. The appearance of new experimental approaches revealed that the generally accepted two excited state (S1 and S2) picture is a drastic simplification of reality. Instead, as much as five other dark states may be located between (or in close vicinity of) the S1 and S2 states, making the excited state dynamics vastly complicated. In photosynthetic systems, carotenoids are crucial constituents of light-harvesting proteins, in which they carry out two rather orthogonal functions. First, there is a conclusive evidence that carotenoids are capable to transfer captured energy to (bacterio)chlorophylls with efficiency ranging from 0-100% [3]. Second, carotenoids serve also as photoprotective agents protecting photosynthetic proteins against excess light. In many systems, carotenoids are capable of carrying out these two functions simultaneously, which makes them rather unique molecules. This contribution summarizes the current knowledge of carotenoid excited state dynamics and aims for answering some questions concerning the roles of dark carotenoid excited states.

[1] T. Polívka, V. Sundström, Chem. Rev. 2004, 104, 2021-2072.
[2] T. Polívka, V. Sundström, Chem. Phys. Lett. 2009, 477, 1-11.
[3] T. Polívka, H. A. Frank, Acc. Chem. Res. 2010, 43, 1125-1134.

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